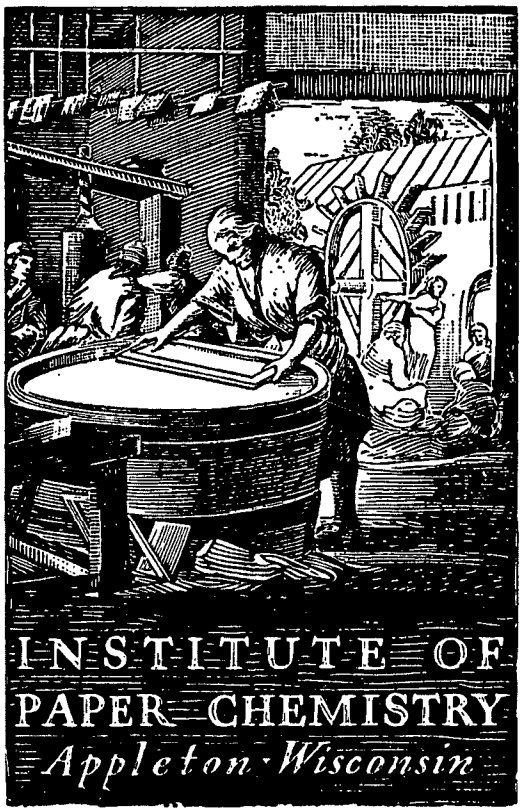

DEGRADATIVE CHANGES IN CARBOHYDRATES OF PULPS FROM OXYGEN-ALKALI REACTIONS

Project 3284

Report Two
A Progress Report
to
MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY

September 30, 1977

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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DEGRADATIVE CHANGES IN CARBOHYDRATES OF PULPS FROM OXYGEN-ALKALI REACTIONS

SUMMARY

Oxygen-alkali red maple (Acer rubrum) pulps and some of the corresponding spent liquors have been analyzed to determine what changes occur in the wood carbohydrates during the pulping process. The pulps, prepared as part of a concurrent pulping study, were generated under both low and high consistency conditions using oxygen-sodium carbonate-sodium bicarbonate and oxygen-sodium carbonate, respectively.

Previously, neutral sugar analyses of the pulps by the alditol acetate method indicated that both pulping processes selectively remove lignin relative to the carbohydrates, and that the degree of selectivity was not very great. The degree of selectivity appeared to be somewhat greater in the low consistency process. The carbohydrate loss in both processes was due primarily to loss of hemicelluloses; loss of cellulose was minimal down to the 65% yield level. Magnesium carbonate at 1% loading (o.d. wood basis) did not affect carbohydrate retention in the high consistency process. Potassium iodide at 10% loading increased carbohydrate retention by 2-3% in the high consistency process. Current neutral sugar analyses show that magnesium acetate at 5% loading and potassium iodide at 10% loading do not affect carbohydrate retention in the low consistency pulping. In addition, limited temperature increases (<20°C) in high and low consistency pulping have a minimal effect on carbohydrate retention at high yield levels. Similarly, varying the oxygen pressure from 60 to 300 psig in high consistency pulping has, at most, a minimal effect on carbohydrate retention at high yield levels.

Ultrafiltration has been used to assess the molecular size of the solids in pulping spent liquors. Additional spent liquor analyses for the high consistency process substantiate the earlier conclusion that a major portion of the carbohydrates removed from the pulp is degraded to low molecular weight (<1000) species. The results are also consistent with a significant part of the material being degraded after dissolution in the pulping liquor, rather than prior to dissolution. Magnesium carbonate does not have an appreciable effect on the degradation; potassium iodide, however, retards the degradation to some extent.

The problems related to gel permeation chromatographic analysis of the carbanilate derivatives of pulp holocelluloses have been circumvented, and the method has been used to determine changes in the degree of polymerization of the wood polysaccharides during pulping. Both the high and low consistency pulping processes cause progressive depolymerization of the wood polysaccharides as the yield decreases. Magnesium carbonate (1%, o.d. wood basis) does not retard the depolymerization, but potassium iodide (10%) drastically reduces the depolymerization in the high consistency process. In the low consistency process, neither magnesium acetate (5%) nor potassium iodide (10%) has any effect on the polysaccharide cleavage reactions. In the absence of degradation inhibitors, depolymerization of the wood polysaccharides is considerably less in the low consistency process than in the high consistency process. Limited temperature increases in the high and low consistency pulping (20°C and 10°C, respectively) do not adversely affect the polysaccharide DP at high yield level. Similarly, increasing the oxygen pressure from 60 to 300 psig does not change the pulp polysaccharide DP values significantly at high yield levels. Chromatographic analyses also showed that oxygen-alkali pulps from red maple can be

bleached without appreciable change in the molecular weight distribution of the polysaccharides.

Future work will involve completion of analyses of kraft pulps prepared from both fiberized and chipped red maple. These analyses are related to the question of carbohydrate damage during fiberization as well as the relative amount of degradation in the kraft and oxygen-alkali processes.

The question of whether gel permeation chromatographic analyses of pulp holocelluloses can be related to cuene viscosities or other pulp properties will also be addressed.

Analyses of selected loblolly pine materials are being initiated to determine whether such analyses present unique problems and also to establish a basis for future work with pine.

In addition, a program directed toward determining approaches to prevent or retard degradation in oxygen-alkali reactions will be defined.

INTRODUCTION

The reactions which the polysaccharides in wood undergo in an oxygen-alkali system are complex and still incompletely understood. Thus, the development of an acceptable high yield oxygen-alkali pulping process in which, of necessity, the carbohydrates must be retained without deleterious degradation, is a formidable challenge (1). This research project was initiated to determine what changes occur in the wood polysaccharides and their relative importance when wood is delignified under various conditions with oxygen in alkaline media (2). The analytical methods being assessed or developed and utilized in Project 3284 permit analysis of the carbohydrates of oxygen-alkali pulps for both retention and degradation as a function of process variables such as time, temperature, yield, oxygen pressure, and additives. The results can potentially be used in directing process conditions toward those which maximize retention of the wood carbohydrates and minimize their degradation.

Information available on reactions of carbohydrates in such systems indicates that the primary concerns from the standpoint of material loss or degradation of the polysaccharides within the fiber are: (a) peeling, or endwise degradation of the polysaccharides; (b) selective removal of hemicelluloses; (c) oxidation of the polysaccharides; and (d) depolymerization, or cleavage of glucosidic linkages of the polysaccharides. These reactions and analytical methods for assessing their importance are discussed in more detail in the initial research proposal (2) and the previous report (3).

Since the last report (3) major emphasis has been on the development of an appropriate procedure for determining wood polysaccharide molecular weight distributions. Degradation of the polysaccharides during derivatization of the holocelluloses was shown to be a problem which had to be circumvented or

minimized. Acceptable derivatization conditions have been determined and utilized in analyses of molecular weight distributions of holocelluloses by gel permeation chromatography (GPC).

Red maple pulps reflecting the effects of additional process variables have been analyzed for neutral sugars. Additional spent liquors from red maple pulps were also fractionated and analyzed for neutral sugars. Work on development of a method for analysis of carboxylic acids in oxygen-alkali pulps was suspended, primarily to allow more time for work on analyses of pulp holocellulose molecular weight distributions.

This report is divided into two sections. The first section pertains to development of the method for determining the molecular weight distribution of wood polysaccharides. The second section summarizes the changes in the carbohydrates of red maple oxygen-alkali pulps as a function of several process variables. Results reported previously (3) are incorporated as necessary to provide continuity or to minimize the necessity of referring to the previous report.

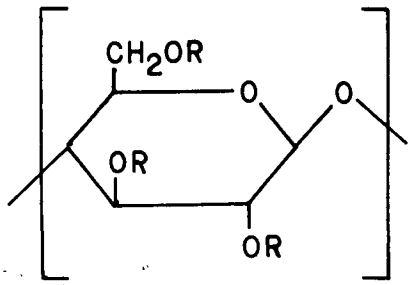
RESULTS AND DISCUSSION

DEGREE OF POLYMERIZATION ANALYSIS — METHOD DEVELOPMENT

General

The major problem in investigating changes in the degree of polymerization (DP) of the wood polysaccharides is conversion of the polysaccharides to derivatives suitable for analysis. Ideally, this should be accomplished without degradation. Basically, two approaches to the problem are available. The wood polysaccharides can be derivatized in the presence of the associated lignin, e.g., direct nitration (4,5), or the lignin can be removed before the polysaccharides are derivatized, i.e., the holocellulose is prepared and then derivatized.

As indicated previously (3), we have been assessing the feasibility of using the carbanilate derivatives of the holocelluloses in conjunction with gel permeation chromatography to determine the molecular weight distribution of wood polysaccharides. The carbanilate derivatives (Fig. 1) have been used in gel permeation chromatographic analyses (GPC) of molecular weight distributions of cellulose (6) and cellulose pulps containing up to 20% hemicellulose (7). The carbanilate derivative is reported to be preferable to the nitrate derivative because the stability of the nitrate, both dry and in solution, is limited and there is risk of degradation of the polysaccharides during nitration (6-8). Also, complete substitution in nitration is difficult to achieve, thus further complicating the interpretation of results (6). Alternatively, carbanilation presumably provides full substitution without degradation of the polysaccharide chain (6-9).



$$R = -\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-C_6H_5$$

Figure 1. Monomer Unit of Cellulose Tricarbanilate

Chromatogram Analysis

A GPC chromatogram of cellulose tricarbanilate prepared from an ICCA-1 pulp (10) is shown in Fig. 2. The details of relating the molecular weight of the polysaccharide percarbanilates to their elution volume (V_i), relative to the elution volume (V_s) of a reference compound (N-phenyl cyclohexyl carbamate), on the basis of the universal calibration concept (11), were described previously (3). In addition, other discussions of the experimental aspects of GPC are available (12,13).

To determine the number-average ($\bar{M}_n$), weight-average ($\bar{M}_w$), and viscosity-average ($\bar{M}_v$) molecular weights from chromatograms, the ordinate heights (h_i) were determined at 2 ml increments of the relative elution volume ($V_s - V_i$) over the entire elution curve (3). The molecular weights (M_i) of cellulose tricarbanilates corresponding to the $V_s - V_i$ values were known from calibration of the chromatographic columns (Fig. 3)*. The number-average molecular weight of the polysaccharide sample was calculated according to Equation (1); the weight-average molecular weight according to Equation (2) (7).

*Since previous reports (3,14) problems associated with the chromatographic system were corrected, and the columns were recalibrated.

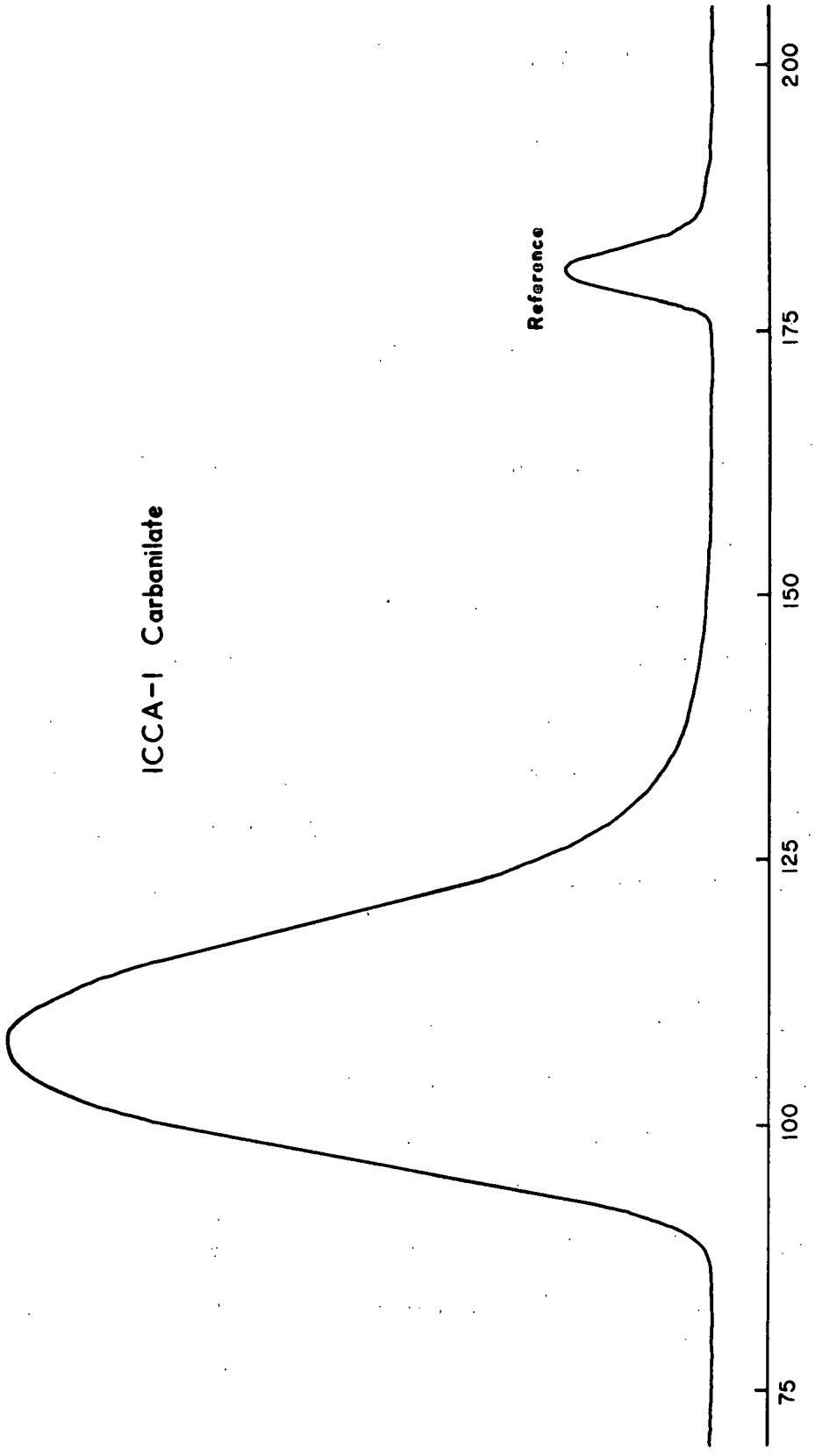


Figure 2. Gel Permeation Chromatogram of Cellulose Tricarbanilate

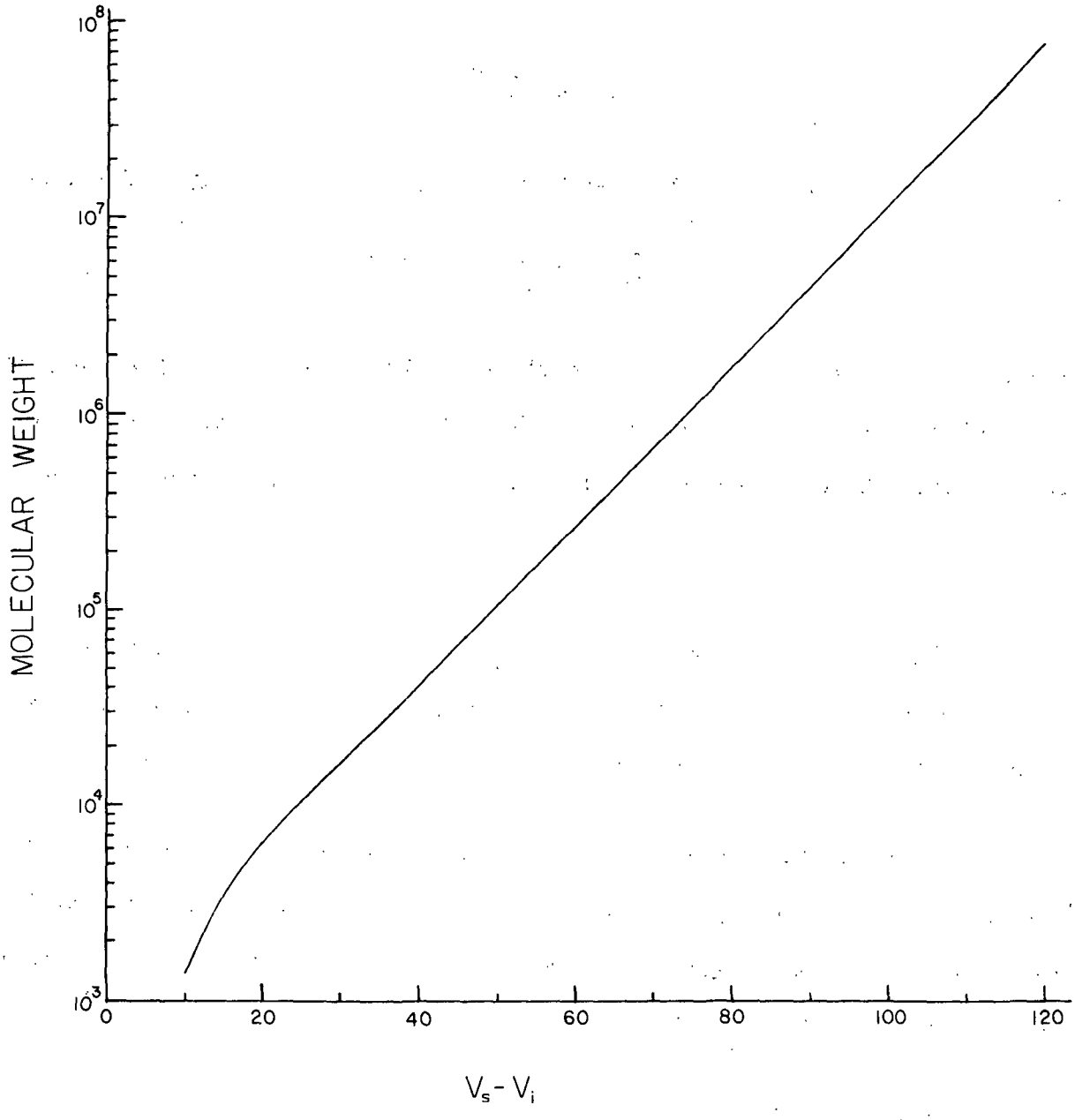


Figure 3. Cellulose Tricarbanilate Molecular Weight Versus Relative Elution Volume ($V_s - V_i$)

$$\overline{M}_n = \sum h_i / \sum (h_i / M_i) \qquad (1)$$

$$\overline{M}_w = \sum h_i M_i / \sum h_i \qquad (2)$$

The viscosity-average molecular weight was calculated according to Equation (3).

$$\overline{M}_v = [\sum h_i M_i^{\alpha} / \sum h_i]^{1/\alpha} \qquad (3)$$

The constant α is the exponential constant of the Mark-Houwink equation [Equation (4)] which relates the intrinsic viscosity of a polymer to its molecular weight. The constants K and α are characteristic for each polymer-solvent combination.

$$[\eta] = KM^{\alpha} \qquad (4)$$

A fourth molecular weight, M_{max}, was defined as the molecular weight corresponding to the point of maximum ordinate height on the high molecular weight portion of the chromatogram.

Apparent number-average DP ($\overline{DP}_n$), weight-average DP ($\overline{DP}_w$), viscosity-average DP ($\overline{DP}_v$), and M_{max} DP (DP_{max}) values were calculated by dividing the respective molecular weight values by the monomer equivalent weight of cellulose tricarbanilate, 519.

Polysaccharide Derivatization

One problem associated with carbanilation of polysaccharides cited in the preceding report is potential degradation of the polysaccharides during derivatization (3). Although such degradation presumably does not occur (6-9), a severe decrease in the DP of cellulose percarbanilate did occur when it was subjected to derivatization reagents, i.e., pyridine solvent and phenyl isocyanate, under reflux conditions (3). Experiments in another laboratory have confirmed this finding (15).

This type of experiment has been repeated utilizing, in addition to reflux conditions, temperatures of 110 and 80°C to determine whether the degradation could potentially be avoided at less drastic derivatization conditions. The results of the experiments are shown in Fig. 4. The results for 110°C and reflux conditons were essentially the same. In addition, deliberately blanketing a reflux reaction with nitrogen to avoid potentially deleterious effects of oxygen did not alter the result. The $\overline{DP}_w$ of the cellulose percarbanilate decreased steadily from ca. 2500 to ca. 650 over 3 days at 110°C and reflux conditions. However, at 80°C the polysaccharide $\overline{DP}_w$ was essentially unchanged for at least two days. Thus, polysaccharide degradation during carbanilation can potentially be avoided by using less drastic reaction conditions than those typically reported in the literature (6-8).

While the decrease in the $\overline{DP}_w$ of the cellulose carbanilate under degradative conditions seems quite severe, the rate of bond cleavage is actually not very great. Calculations based on Equation (5) (16) which relates the change in the $\overline{DP}_n$ of the polymer to the rate of bond cleavage yielded a rate constant k of ca. 1.3×10^{-8} sec^{-1} which corresponds to a bond half-life of ca. 1.7 years.

$$(1/\overline{DP}_{n,o}) - (1/\overline{DP}_{n,t}) \simeq kt \qquad (5)$$

A second potential problem area with the carbanilation procedure, particularly with holocelluloses, is completeness of substitution and selective derivatization. To determine whether complete substitution of the holocellulose polysaccharides can be effected with the milder reaction conditions which do not degrade the polysaccharides, several holocellulose carbanilates and cellulose carbanilate prepared using the nondegradative reaction conditions were analyzed for their nitrogen content. The results are shown in Table I in which the

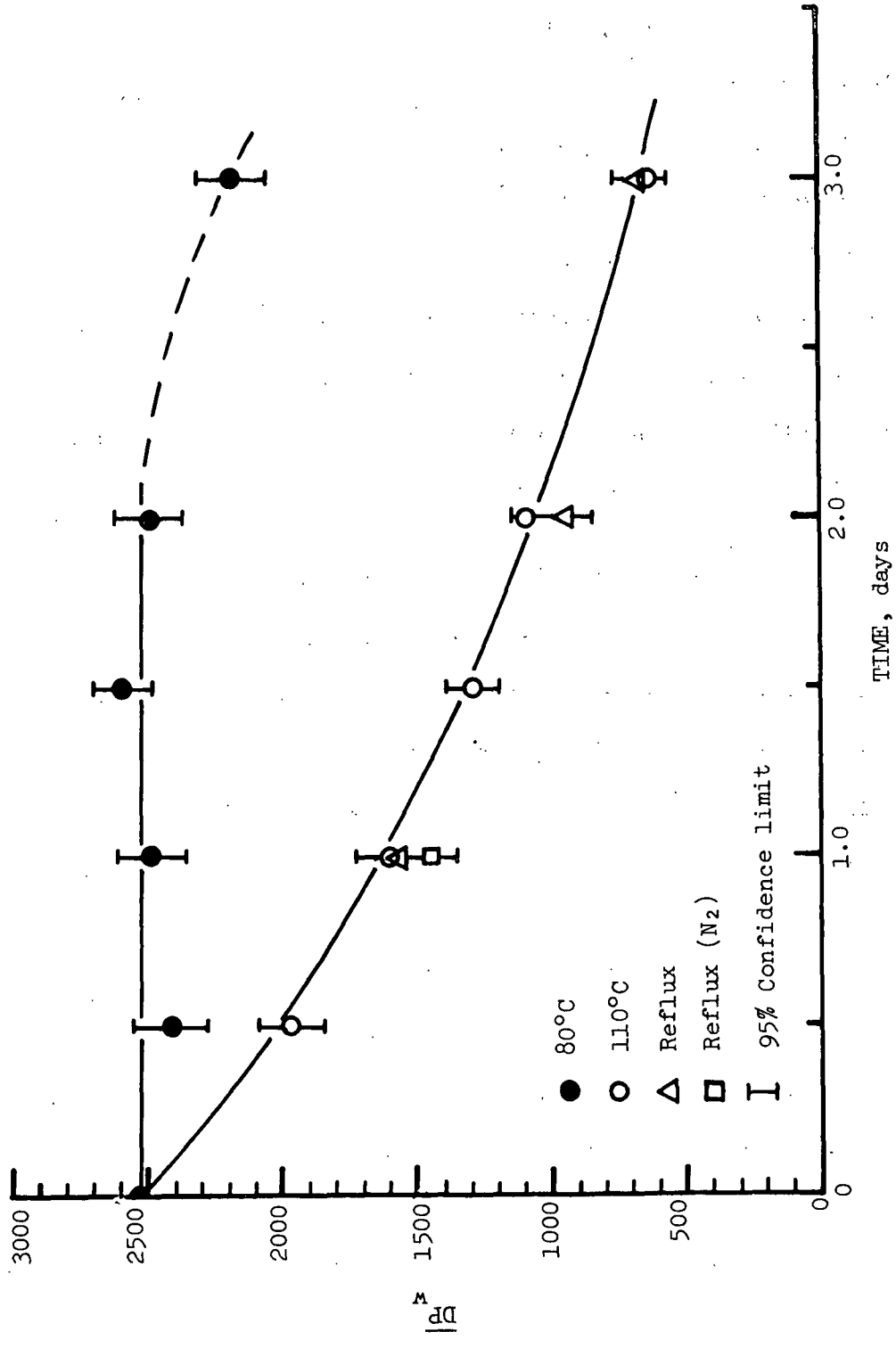


Figure 4. Cellulose Tricarbanilate Stability Under Carbanilation Conditions Using Pyridine Solvent

nitrogen analyses, and the corresponding degrees of substitution (DS), are compared to theoretical values based on normalized carbohydrate analyses of the corresponding pulps. The analytical values are reasonably close to the theoretical values, thus indicating that substitution of the polysaccharides is essentially complete. In addition, the data provides a fair indication that the carbanilated polysaccharides are representative of the polysaccharides in the initial pulp.

TABLE I

NITROGEN ANALYSES OF CELLULOSE AND HOLOCELLULOSE CARBANILATES[a,b]

	Nitrogen, %		DS	
	Analyzed	Theoretical[c]	Analyzed	Theoretical[c]
Cellulose	8.17	8.09	3.03	3.00
FRM	7.67	7.96	2.61	2.71
AT-FRM	8.02	7.97	2.75	2.73
HC-80	7.96	7.98	2.76	2.77
HC-72	8.19	8.00	2.85	2.79
HC-65	7.82	8.01	2.75	2.82

[a] Chlorine-ethanolamine holocelluloses (3).

[b] FRM, fiberized red maple; AT-FRM, sodium hydroxide-treated FRM (90% yield); HC, high consistency process pulp, number after the hyphen is the approximate pulp yield on an o.d. FRM basis.

[c] A value of less than 8.09% N or a DS of less than 3.0 reflects the presence of pentose based hemicelluloses in the polysaccharide mixture. Theoretical values for nitrogen content and DS are based on normalized carbohydrate analyses of the pulps.

Effect of Holocellulose Preparation

Ideally, an isolation of holocellulose should effect complete removal of lignin without loss or degradation of polysaccharidic components. However, the available methods for such delignification lead to some depolymerization of

the polysaccharides (17). Of the available methods for preparing holocelluloses, the chlorine-ethanolamine procedure described previously (3) is preferred for quantitative isolation of holocellulose (17,18). The disadvantage of the chlorine-ethanolamine procedure is that it is very tedious and time consuming. From the standpoint of being utilized in a routine analytical procedure, the acid-chlorite procedure (3) typically used for viscosity measurements is more suitable because of its simplicity and the possibility of treating several samples simultaneously. Therefore, we have done a limited study of the effect of holocellulose preparation on the apparent DP of the wood polysaccharides. The results are presented in Table II.

When the lignin content of the sample is very high, e.g., FRM and AT-FRM (Table II), the DP values obtained from the acid-chlorite and chlorine-ethanolamine holocelluloses are drastically different, with the acid-chlorite holocellulose yielding much lower values. However, with samples of lower lignin content the DP values obtained from the two holocelluloses are comparable. The result cannot be reasonably attributed to excessive degradation in the acid-chlorite system since all the samples were treated similarly. In addition, if this were the case, it might be anticipated that carbohydrate degradation would be most severe in the samples containing the least amount of lignin. Rather, the differences in the DP values may be attributable to inaccessibility of the carbohydrates to the derivatization reagents in the acid-chlorite holocellulose due to incomplete delignification. This is consistent with the very low yields of polysaccharide carbanilates derived from acid-chlorite holocelluloses of FRM and AT-FRM. On this basis, the problem might be eliminated by multiple acid-chlorite treatments of samples with high lignin contents. This has not been tried yet.

TABLE II

EFFECT OF HOLOCELLULOSE PREPARATION[a,b] ON THE OBSERVED DEGREE OF POLYMERIZATION

	Neutral Carbohydrate, %	Holocellulose Method[c]	$\overline{DP}_w$	DP_{max}
FRM	65	C	2000	2720
		AC	1340	860
AT-FRM	66	C	1930	2830
		AC	1260	1420
HC-72	74	C	1450	840
		AC	1560	830
HC-72-Mg	75	C	1360	770
		AC	1550	790
LC-68-Mg	80	C	1710	1110
		AC	1670	1180
HC-65	82	C	1430	730
		AC	1460	740
HC-65-KI	85	C	1740	1240
		AC	1790	1220

[a] FRM, fiberized red maple; AT-FRM, sodium hydroxide-treated FRM (90% yield); HC and LC indicate high consistency and low consistency processes, respectively; Mg and KI indicate magnesium acetate and potassium iodide additives, respectively; numbers after hyphens are the approximate pulp yield on an o.d. FRM basis.

[b] Project 3264 code numbers: HC-72, 19C; HC-72-Mg, 22C; HC-65, 65C; HC-65-KI, 69C; and LC-68-Mg, 37.

[c] C, chlorine-ethanolamine procedure; AC, acid-chlorite procedure.

Reproducibility

The average standard deviation for replicate $\overline{DP}_w$ analyses of the same carbanilate preparation was 2.7% of the mean $\overline{DP}_w$ for all holocellulose and cellulose samples analyzed. For a limited number of analyses, the average standard deviation of the mean $\overline{DP}_w$ for replicate carbanilations of the same

holocellulose or cellulose was 3.0%. The reproducibility of the holocellulose preparation has not been investigated.

DEGRADATIVE CHANGES IN OXYGEN-ALKALI PULPS FROM RED MAPLE

General

Materials utilized in the project have been prepared as an integral part of a concurrent oxygen-alkali pulping project, Project 3264. The materials include fiberized red maple (Acer rubrum) chips (FRM) (19), fiberized chips which have been treated with sodium hydroxide (AT-FRM), pulps prepared at various yield levels at both high consistency (HC) standard conditions employing sodium carbonate as the base and low consistency (LC) standard conditions employing sodium carbonate and sodium bicarbonate, and pulps prepared using magnesium carbonate (Mg), magnesium acetate (Mg), and potassium iodide (KI) as degradation inhibitors.

Alkali pretreated fiberized chips (AT-FRM) were prepared by treating fiberized red maple chips (FRM) with 5% sodium hydroxide (o.d. FRM basis) at 10% consistency for 30 minutes at 90°C. The yield of AT-FRM was approximately 90%.

In the high consistency (HC) process a liquor-to-wood ratio of ca. 3:1 with ca. 25 g/liter sodium carbonate (Na_2CO_3) was used. The starting material for the process was AT-FRM. Reaction temperatures of 120 to 140°C and oxygen pressures of 60 to 130 psig (at 100°C) were employed. Yields (o.d. FRM basis) ranged down to ca. 65%.

In the low consistency (LC) process, a liquor-to-wood ratio of ca. 70:1 with ca. 7.5 g/liter sodium bicarbonate ($NaHCO_3$) and 10 g/liter sodium carbonate (Na_2CO_3) was used. The pulping liquor was continuously circulated through the starting material (FRM) which was held stationary. Reaction temperatures of

120 and 130°C with 3000 psig air pressure were employed. Yields (o.d. FRM basis) ranged down to ca. 65%.

Analysis of Carbohydrate Losses

The amount of carbohydrate lost from wood or pulp during processing can be obtained from yield data for the process in conjunction with analyses of the sugars in the materials after hydrolysis of the polysaccharides. In addition, this type of analysis can indicate whether a particular type of polysaccharide is being selectively removed during processing. This type of analysis has been used quite successfully in determining the importance of carbohydrate losses in the low and high temperature regions of the kraft process (20).

Previous neutral sugar analyses of red maple pulps (3) indicated that in both the high and low consistency pulping processes lignin is selectively removed relative to the carbohydrates, but the degree of selectivity is not very great. The degree of selectivity appears to be somewhat greater in the low-consistency process. Of the carbohydrates lost during pulping, hemicelluloses are selectively removed relative to cellulose. The loss of cellulose is minimal down to the 65% yield level for both processes.

Earlier analyses also indicated that magnesium carbonate at 1% loading (o.d. wood basis) does not affect carbohydrate retention in the high consistency pulping. Potassium iodide at 10% loading did increase carbohydrate retention, but at a practical level of addition the effect would be very small.

Recent analyses have centered on pulps which potentially reflect the effect of degradation inhibitors on the low consistency process, the effect of temperature on both the high and low consistency processes, and the effect of oxygen pressure in the high consistency process. Unfortunately, the available

pulps which can potentially reflect changes in carbohydrate retention as a function of temperature and oxygen pressure for the high consistency process are high yield pulps. Thus, potential differences would not be magnified to the extent that they would be at lower yields, i.e., at greater carbohydrate loss.

The data in Table III indicate that the depolymerization inhibitors, 5% magnesium acetate and 10% potassium iodide, have no significant effect on the amount of carbohydrate retained in the low consistency process at the 68 and 65% yield levels, respectively.

TABLE III

EFFECT OF DEGRADATION INHIBITORS ON CARBOHYDRATE RETENTION[a] IN THE LOW CONSISTENCY PROCESS

Additive[a]	Pulp Yield[a]	Temp., °C	Glucan	Xylan	Mannan	Galactan	Arabinan	Total Glycan
--	68	120	44.6	9.8	1.2	0.1	0.3	56.0
5% $Mg(OAc)_2$	68	120	43.2	9.8	1.2	0.1	0.4	54.7
--	64	130	41.5	8.5	1.0	0.1	0.4	51.5
10% KI	65	130	41.0	9.0	1.2	0.3	0.5	52.0

[a]Weight percent, o.d. FRM basis.

An increase in the reaction temperature decreases the time required to reach a given yield level. Thus, the question of whether the reaction temperature affects the amount of carbohydrates retained at a given yield level is a very practical one. The neutral sugar analyses in Table IV indicate that effects of a 10°C increase in the low consistency process and a 20°C increase in the high consistency process at the 70 and 80% yield levels, respectively, are probably quite small.

TABLE IV

EFFECT OF TEMPERATURE ON CARBOHYDRATE RETENTION[a]
IN THE LOW AND HIGH CONSISTENCY PROCESSES

Process[b]	Temp., °C	Pulp Yield[a]	Glucan	Xylan	Mannan	Galactan	Arabinan	Total Glycan
LC	120	70	44.5	10.0	1.2	0.1	0.3	56.1
LC	130	71	42.4	9.3	1.5	0.4	0.4	54.1
HC	120	80	43.7	10.6	2.0	0.5	0.6	57.5[c]
HC	140	81	42.5	11.4	1.3	0.5	0.6	56.3

[a] Weight percent, o.d. FRM basis.

[b] LC, low consistency; HC, high consistency.

[c] Includes 0.1% rhamnan.

Since increased oxygen pressure can also accelerate the delignification process, its effect on carbohydrate retention at a given yield level is also of importance. The neutral sugar analyses in Table V indicate that varying the initial oxygen pressure from 60 to 300 psig (100°C) in the high consistency process does not affect the yield of carbohydrate significantly at the 80% pulp yield level.

TABLE V

EFFECT OF OXYGEN PRESSURE ON CARBOHYDRATE RETENTION[a]
IN THE HIGH CONSISTENCY PROCESS

Oxygen Pressure, psig[b]	Pulp Yield[a]	Glucan	Xylan	Mannan	Galactan	Arabinan	Total Glycan
60	81	44.7	11.8	1.6	0.5	0.7	59.3
130	80	43.7	10.6	2.0	0.5	0.6	57.5[c]
300	80	43.4	11.4	1.5	0.3	0.6	57.2

[a] Weight percent, o.d. FRM basis.

[b] At 100°C.

[c] Includes 0.1% rhamnan.

Spent Liquor Analyses

The loss of carbohydrate from wood or pulp during alkaline processes is not necessarily due only to the peeling reaction in which the polysaccharides are degraded to acidic monomeric units. Polysaccharides with a low degree of polymerization, particularly if they possess acidic functional groups, can dissolve in an alkaline liquor without prior degradation. One potential method of estimating the molecular size of the carbohydrates in a spent liquor, and thus assessing the relative importance of peeling versus dissolution, is ultrafiltration in conjunction with sugar analyses.

Previously we had fractionated high consistency process spent liquors from 72% yield pulps by ultrafiltration and analyzed the high molecular fractions for neutral sugars (3). The results indicated that a major portion of the carbohydrates removed from the pulp in the high consistency process is degraded to low molecular weight (<1000) species and that magnesium carbonate inhibitor does not have an appreciable effect on the degradation.

We have extended this type of analysis to high consistency process spent liquors corresponding to 65% yield pulps prepared with and without degradation inhibitors. The results of the analyses are tabulated in Table VI, along with the previous results.

At the 65% yield level (HC-65, HC-65-Mg, and HC-65-KI liquors) approximately 40% of the material lost from the pulp in the two stages was of sufficient molecular size to be retained on a UM-10 membrane. This is about 60% of the UM-10 retention at the 72% yield level and is consistent with a significant part of the material being degraded after dissolution in the pulping liquor, rather than prior to dissolution.

TABLE VI

SPENT LIQUOR ANALYSES

Liquor Source[a,b]	Stage	Retention, % of liquor solids		Retention,[c] % of pulp loss		UM-10 Neutral Glycan Analyses (wt.% of v.d. solids)[c,d]						
		UM-10	UM-2	UM-10	UM-2	Total	Glucan	Xylan	Mannan	Galactan	Arabinan	Rhamnan
AT-FRM	--	37[e]	2	50	3	26.2	1.7	15.7	1.1	3.7	2.0	2.0
		36[e]	4	50	6	--	--	--	--	--	--	--
HC-80[f]	--	57	12	77	15	20.5	0.4	15.9	0.2	0.8	2.6	0.6
HC-72[g]	1st	59	10	33	6	16.8	0.2	13.5	0.1	0.6	2.0	0.4
	2nd	54	7	31	4	11.8	0.1	8.9	0.1	0.6	1.8	0.3
HC-72-Mg[g]	1st	46	3	32	4	21.1	0.2	16.5	0.4	0.8	2.4	0.8
	2nd	47	11	25	6	13.0	0.2	9.5	0.1	0.6	2.1	0.5
HC-65[h]	1st	30	13	15	7	15.5	0.4	10.5	0.3	1.2	2.4	0.7
	2nd	36	13	21	8	9.7	0.4	6.0	0.2	1.0	1.8	0.3
HC-65-Mg[h]	1st	31	14	15	8	20.6	0.3	14.8	0.2	1.5	3.1	0.7
	2nd	39	15	22	9	10.9	0.1	7.5	0.1	0.9	2.0	0.3
HC-65-KI[h]	1st	26	14	13	8	15.1	0.2	9.1	0.2	1.9	2.7	1.0
	2nd	42	11	26	7	10.8	0.1	6.5	0.1	1.4	2.3	0.4

[a] FRM, fiberized red maple chips; AT-FRM, sodium hydroxide treated FRM; HC and LC designated high and low consistency, respectively; Mg and KI indicate magensium carbonate and potassium iodide additives, respectively.

[b] Project 3264 code numbers: HC-80, 11C; HC-72, 19C; HC-72-Mg, 22C; HC-65, 39C; HC-65-Mg, 42C and 65C; HC-65-KI, 69C.

[c] Weights of retained solids are corrected for ash contents.

[d] v.d., vacumn dried over phosphorus pentoxide.

[e] Includes material retained on the 0.45 micron filter also.

[f] One 4-hour stage.

[g] Two 4-hour stages.

[h] Two 7-hour stages.

Based on a nominal molecular weight cut-off limit of 10,000 for the UM-10 membrane (21), the degree of polymerization of retained polysaccharides (primarily xylan, see Table VI), if unassociated with lignin, would have to be greater than ca. 70. However, based on neutral sugar analyses, even with allowances made for unanalyzed uronic acids, less than 25% of the UM-10 retentates from the spent liquors are carbohydrate. Based on neutral sugar analyses in Table VI and those reported previously for the corresponding pulps (3), ca. 20, 27, and 42% of the carbohydrates lost in preparing pulps HC-65, HC-65-Mg and HC-65-KI from AT-FRM are accounted for in the UM-10 retentates of the respective spent liquors. As found for the 72% yield level, the quantity of UM-2 retentate at the 65% yield level is small. Therefore, as noted previously (3), a significant portion of the polysaccharides removed during pulping are degraded to very low molecular weight species. Magnesium carbonate in the pulping liquor does not significantly affect the result. However, potassium iodide does increase the percentage of carbohydrate in the high molecular weight fraction, consistent with the postulate that a significant portion of the polysaccharides are degraded after dissolution in the pulping liquor.

Degree of Polymerization Analyses

Chlorine-ethanolamine holocellulose of the red maple pulps were used to determine the polysaccharide DP distributions. The holocelluloses were carbanilated under the nondegradative conditions described earlier. Representative normalized molecular weight distributions generated from liquid chromatographic analysis of two holocellulose percarbanilates are shown in Fig. 5. One distribution is from an analysis of fiberized chips (FRM), the other is from a 66% yield pulp (HC-66) prepared by the high consistency process.

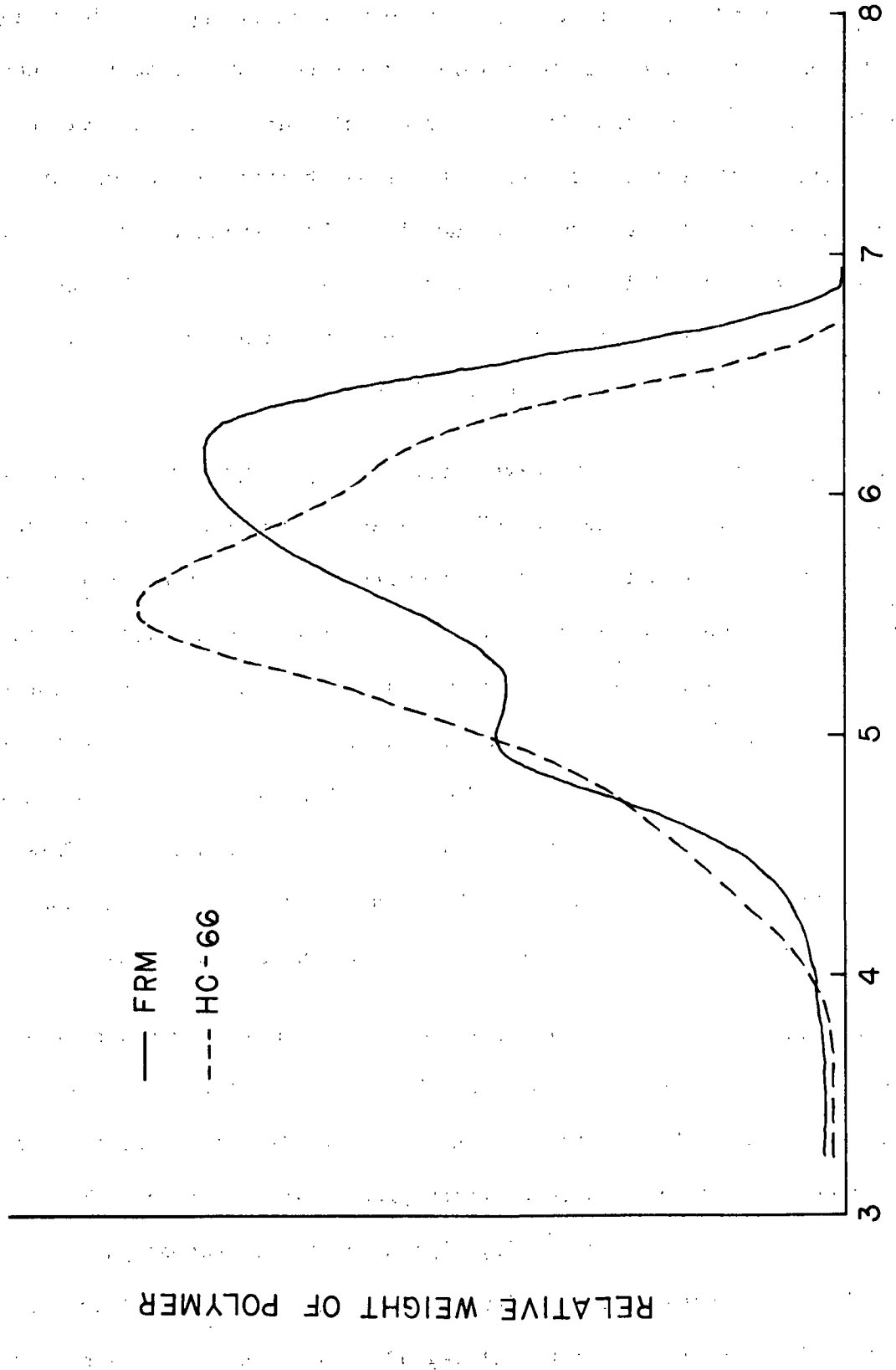


Figure 5. Normalized Molecular Weight Distributions of Polysaccharides in Fiberized Red Maple Chips (FRM) and a 66%-Yield Oxygen-Sodium Carbonate Pulp (HC-66) from FRM

The utility of the analytical procedure is readily apparent from Fig. 5. Qualitative differences in the molecular weight distributions are obvious immediately. The FRM holocellulose exhibits two maxima which are indicative of the cellulose and hemicellulose constituents. The lesser hemicellulose content of the HC-66 holocellulose is quite obvious. In addition, the overall molecular weight values for the HC-66 holocellulose are lower than those for the FRM holocellulose. This is indicative of the depolymerization of the polysaccharides occurring during the oxygen-sodium carbonate pulping process.

Several aspects of the two oxygen-alkali pulping processes are apparent from the quantitative data derived from GPC analyses. The first of this data (Table VII) indicates, as expected, that in the absence of degradation inhibitors both the high and low consistency processes cause progressive depolymerization of the polysaccharides as the yield decreases. This is manifested as a continual decrease in the DP_{max}, $\overline{DP}_w$, and $\overline{DP}_v$ values with decreasing yield. For example, compare these values for the series FRM, AT-FRM, HC-80, HC-72, and HC-66. However, the $\overline{DP}_n$ does not change drastically down to the 65% yield level. This apparently reflects the opposing effects of removal of low DP materials through dissolution and formation of low DP material through depolymerization.

It has been reported that the low consistency process degrades the wood polysaccharides to a lesser extent than the high consistency process at comparable yield levels. For example, the cuene holocellulose viscosity of a 66% yield pulp produced by the low consistency process was reported to be 9.9 cp whereas the viscosity of the corresponding high consistency process pulp was 6.6 cp (22). This is substantiated by GPC analyses of the holocelluloses as shown in Table VIII. The lesser degree of degradation in the low consistency process is reflected in the greater values of DP_{max}, $\overline{DP}_w$, and $\overline{DP}_v$ of pulp LC-66 relative to pulp HC-66.

TABLE VII

CHANGE OF POLYSACCHARIDE DP WITH PULP YIELD[a,b,c,d]

	Pulp Yield[e]	DP_{max}	$\overline{DP}_w$	$\overline{DP}_v$	$\overline{DP}_n$
FRM	--	2720	2000	1920	230
AT-FRM	90	2900	1930	1850	240
HC-80	80	1020	1620	1550	230
HC-72	72	840	1450	1390	200
HC-66	66	650	1230	1170	200
LC-71	71	1130	1830	1760	250
LC-64	64	780	1470	1400	230

[a] FRM, fiberized red maple; AT-FRM, sodium hydroxide-treated FRM; HC and LC designate preparation by the high and low consistency processes, respectively.
[b] HC, 120°C pulping temperature; LC, 130°C.
[c] Project 3264 code numbers: HC-80, 11C; HC-72, 19C; HC-66, 39C; LC-71, 129; and LC-64, 133.
[d] Chlorine-ethanolamine holocelluloses (3).
[e] Oven-dry FRM basis.

TABLE VIII

EFFECT OF PULPING PROCESS ON POLYSACCHARIDE DP[a,b,c]

	DP_{max}	$\overline{DP}_w$	$\overline{DP}_v$	Cuene Viscosity, cp[d]
FRM	2720	2000	1920	16.7
HC-66	650	1230	1170	6.0
LC-66	950	1640	1580	8.7

[a] Chlorine-ethanolamine holocelluloses (3).
[b] Pulping temperature was 120°C for both processes.
[c] FRM, fiberized red maple; HC and LC, high and low consistency processes, respectively; numbers after the hyphen are the pulp yield on an o.d. FRM basis.
[d] Determined on chlorine-ethanolamine holocelluloses.

Compounds such as magnesium carbonate (23) and potassium iodide (24) have been added to oxygen-alkali processes in an attempt to inhibit depolymerization of the wood polysaccharides, particularly cellulose. It was previously reported, on the basis of pulp evaluations (22), that addition of magnesium carbonate did not retard polysaccharide depolymerization in the pulping of red maple by the high consistency process. This is substantiated by the DP analyses shown in Table IX. At both the 72% yield level (HC-72 vs. HC-72-Mg) and the 65% yield level (HC-66 vs. HC-65-Mg) the DP_{max}, $\overline{DP}_w$, $\overline{DP}_v$, and $\overline{DP}_n$ values for the pulps prepared with and without magnesium carbonate are essentially the same. In addition, the normalized molecular weight distributions of pulp HC-66 and HC-65-Mg are virtually identical as shown in Fig. 6.

TABLE IX

EFFECT OF MAGNESIUM COMPOUNDS ON POLYSACCHARIDE DP[a,b,c,d]

	Additive[e]	DP_{max}	$\overline{DP}_w$	$\overline{DP}_v$	$\overline{DP}_n$
HC-72	--	840	1450	1390	200
HC-72-Mg	1% $MgCO_3$	770	1360	1300	200
HC-66	--	650	1230	1170	200
HC-65-Mg	1% $MgCO_3$	690	1290	1230	210
LC-70	--	1160	1830	1750	250
LC-69-Mg	5% $Mg(OAc)_2$	1100	1710	1630	230

[a] Chlorine-ethanolamine holocelluloses (3).
[b] HC and LC, high and low consistency processes, respectively; numbers after the hyphen are the pulp yield on an o.d. FRM basis.
[c] HC, 120°C pulping temperature; LC, 130°C.
[d] Project 3264 code numbers: HC-72, 19C; HC-72-Mg, 22C; HC-66, 39C; HC-65-Mg, 42C and 65C; LC-70, 35/38C; and LC-69-Mg, 37.
[e] Ovendry FRM basis.

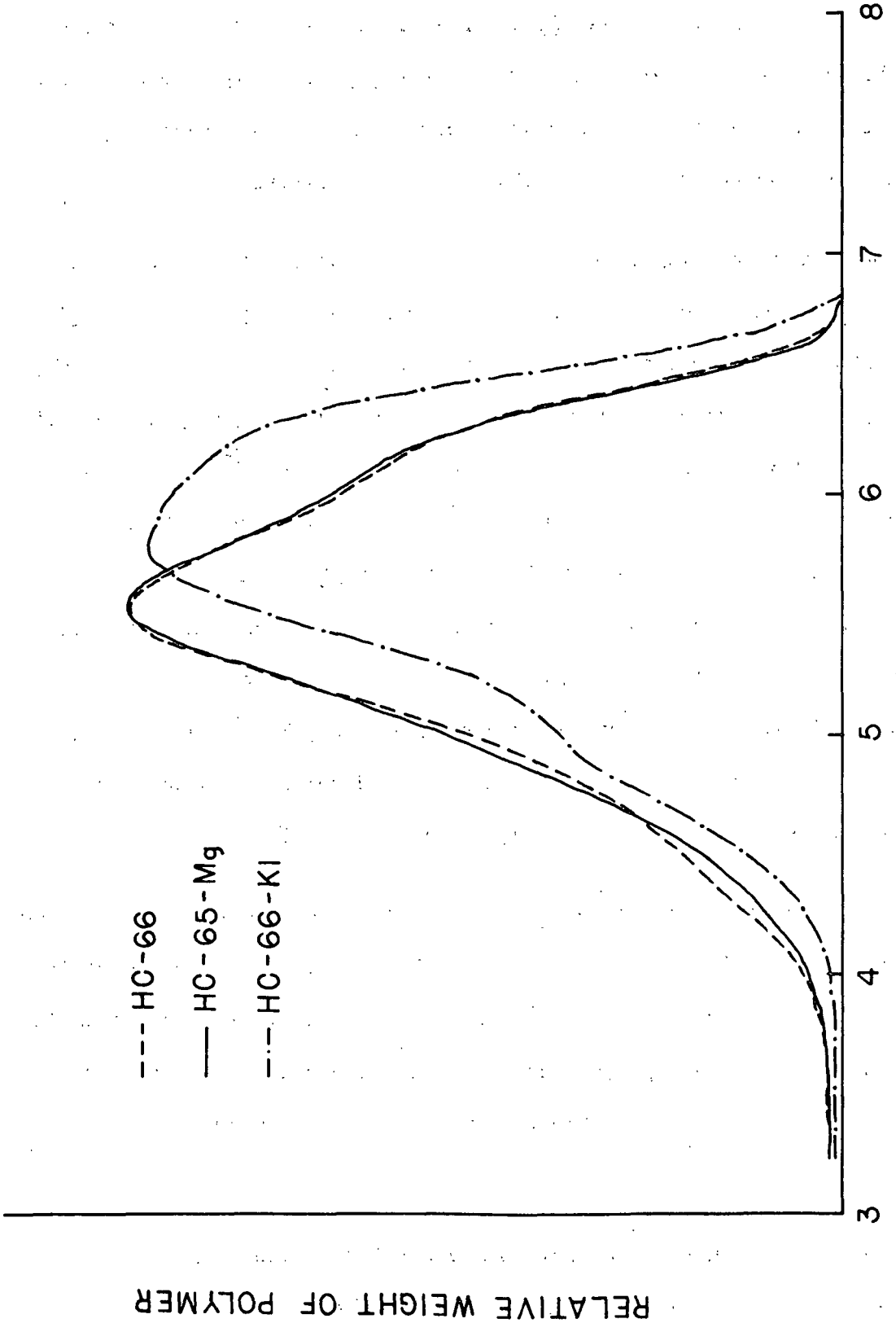


Figure 6. Normalized Molecular Weight Distributions of Polysaccharides in 65%-Yield High Consistency Process Pulps from FRM: HC-66, No Additive; HC-65-Mg, 1% $MgCO_3$ Additive; and HC-66-KI, 10% KI Additive

Similarly, it was reported that magnesium acetate had no beneficial effect in the low consistency process (25). This is also substantiated by the GPC data in Table IX. At the 69% yield level (LC-70 vs. LC-69-Mg) the DP values for the pulp prepared with magnesium acetate additive are not substantially different from those for the pulp prepared without the additive.

In contrast to the magnesium additives, addition of potassium iodide inhibitor to the high consistency process led to upgraded pulp properties (22). The DP_{max} of a 66% yield pulp produced with potassium iodide additive (HC-66-KI) was considerably greater (by ca. 600) than that of a 66% yield pulp prepared without the inhibitor (HC-66) (Table X). In addition, the $\overline{DP}_w$ and $\overline{DP}_v$ of HC-66-KI are considerably greater than those of HC-66, consistent with the respective pulp cuene holocellulose viscosities of 15.6 and 6.5 cp (22). The fact that the $\overline{DP}_n$ of HC-66-KI is greater than that of both HC-66 and AT-FRM indicates that some low DP material (hemicelluloses) has been removed without concomitant formation of appreciable low DP polysaccharides through depolymerization. The ability of potassium iodide to inhibit polysaccharide depolymerization in the high consistency process is illustrated graphically in Fig. 6.

In the low consistency process potassium iodide had no beneficial effect on pulp properties at the 65% yield level (25). This is similarly reflected in the DP values obtained by GPC analyses which are shown in Table X. The inability of potassium iodide to retard depolymerization in the low consistency process is probably due to dilution of the inhibitor by the increased amount of cooking liquor.

The question of whether the pulping temperature affects the polysaccharide DP at a given yield level is very pertinent since increasing the reaction temperature decreases the time required to reach a specified yield

level. The DP analyses in Table XI indicate that a 10°C increase in the low consistency process and a 20°C increase in the high consistency process at the 70 and 80% yield levels, respectively, do not adversely affect the polysaccharide DP values. Whether significant differences would be manifested at much lower yield levels is unknown.

TABLE X

EFFECT OF POTASSIUM IODIDE ON POLYSACCHARIDE DP[a,b,c]

	Additive[d]	DP_{max}	$\overline{DP}_w$	$\overline{DP}_v$	$\overline{DP}_n$	Cuene Viscosity, cp[e]
AT-FRM	--	2900	1930	1850	240	--
HC-66	--	650	1230	1170	200	6.5
HC-66-KI	10% KI	1240	1740	1680	320	15.6
LC-64	--	780	1470	1400	230	7.5
LC-65-KI	10% KI	710	1410	1340	220	9.2

[a]Chlorine-ethanolamine holocelluloses (3).
[b]Project 3264 code numbers: HC-66, 39C; HC-66-KI, 69C; LC-64, 133; and LC-65-Ki, 132.
[c]HC-120°C pulping temperature; LC, 130°C.
[d]Oven-dry FRM basis.
[e]Determined on acid-chlorite holocelluloses (25).

TABLE XI

EFFECT OF TEMPERATURE ON POLYSACCHARIDE DP[a,b]

Process	Temp., °C	Pulp Yield[c]	DP_{max}	$\overline{DP}_w$	$\overline{DP}_n$
LC	120	70	1160	1830	250
LC	130	71	1130	1830	280
HC	120	80	1020	1620	230
HC	140	79	1160	1750	250

[a]Chlorine-ethanolamine holocelluloses.
[b]Project 3264 code numbers: LC-120°C, 35/38C; LC-130°, 129; HC-120°, 11C; and HC-140°, 80.
[c]Oven-dry FRM basis.

Similarly, since increased oxygen pressure can also accelerate the delignification process, its effect on carbohydrate degradation at a given yield level is also of importance. The data in Table XII indicate that varying the initial oxygen pressure from 60 to 300 psig (at 100°C) does not change the polysaccharide DP values significantly at the 80% yield level in the high consistency process.

TABLE XII

EFFECT OF OXYGEN PRESSURE ON POLYSACCHARIDE DP[a]
IN THE HIGH CONSISTENCY PROCESS

Oxygen, psig[d]	Pulp Yield[e]	DP_{max}	$\overline{DP}_w$	$\overline{DP}_n$
60	81	1230	1830	250
130	80	1020	1620	230
300	80	1080	1740	250

[a]Chlorine-ethanolamine holocelluloses (3).
[b]120°C pulping temperature.
[c]Project 3264 code numbers: 60 psig, 95 and 99; 130 psig, 11C; and 300 psig, 104.
[d]At 100°C.
[e]Oven-dry FRM basis.

Another question of importance is whether oxygen-alkali pulps can be bleached without extensive degradation of the polysaccharides. Limited data on the effect of bleaching on the polysaccharide of pulps prepared by the high consistency process are presented in Table XIII. Two 65% yield pulps, one prepared with no additive and the other prepared with 10% potassium iodide additive, were bleached using DEDP stages (22). As indicated by the similarity of the DP values, no appreciable change in the molecular weight distribution of the polysaccharides of either pulp occurred during bleaching.

TABLE XIII

EFFECT OF BLEACHING ON POLYSACCHARIDE DP[a,b,c,d]

	DP_{max}	$\overline{DP}_w$	$\overline{DP}_v$	$\overline{DP}_n$
HC-65	730	1430	1360	190
HC-65-Bl	680	1380	1310	210
HC-65-KI	1240	1740	1680	320
HC-65-KI-BL	1120	1890	1810	260

[a] Chlorine-ethanolamine holocelluloses.

[b] HC, high consistency; BL, bleached; KI, potassium iodide additive.

[c] DEDP bleach stages.

[d] Project 3264 code numbers: HC-65, 65C and HC-65-KI, 69C.

CONCLUSIONS

Varying the oxygen pressure in high consistency pulping of red maple from 60 to 300 psig has, at most, a minimal effect on carbohydrate retention at high yield levels. Limited temperature increases (<20°C) in high and low consistency pulping have a minimal effect on carbohydrate retention at high yield levels.

Magnesium acetate at 5% loading (o.d. wood basis) and potassium iodide at 10% loading do not affect carbohydrate retention in the low consistency pulping.

Additional spent liquor analyses for the high consistency process substantiate the earlier conclusion that a major portion of the carbohydrate removed from the pulp is degraded to low molecular weight (<1000) species. The results are also consistent with a significant part of the material being degraded after dissolution in the pulping liquor, rather than prior to dissolution. Potassium iodide retards the degradation, while magnesium carbonate has little, if any, effect.

Gel permeation chromatographic analysis of the carbanilate derivatives of pulp holocelluloses can be used for determining changes in the degree of polymerization of wood polysaccharides during pulping. Based on such analyses, both the high and low consistency pulping processes cause progressive depolymerization of the wood polysaccharides as the yield decreases. Magnesium carbonate (1%, o.d. wood basis) does not retard the depolymerization, but potassium iodide (10%) drastically reduces the depolymerization in the high consistency process. In the low consistency process, neither magnesium acetate (5%) or potassium iodide (10%) have any effect on the depolymerization. In the

absence of degradation inhibitors, depolymerization of the wood polysaccharides is considerably less in the low consistency process than in the high consistency process. Limited temperature increases in the high and low consistency pulping (20 and 10°C, respectively) do not adversely affect the pulp polysaccharide DP values at high yield levels. Similarly, increasing the oxygen pressure in high consistency pulping from 60 to 300 psig does not change the pulp polysaccharide DP values significantly at high yield levels. Oxygen-alkali pulps from red maple can be bleached without appreciable change in the molecular weight distribution of the polysaccharides.

FUTURE WORK

Analyses on kraft pulps prepared from both fiberized and chipped red maple will be completed. These analyses are related to the question of carbohydrate damage during fiberization as well as the relative amount of degradation in the kraft and oxygen-alkali processes.

Potential relationships between gel permeation chromatographic analyses of pulp holocelluloses and other pulp properties will be examined.

Analyses are currently being initiated on selected loblolly pine materials. The initial work will determine whether analysis of the pine presents unique problems and also establish a basis for future work with the pine.

In addition, a program directed toward preventing or retarding degradation in oxygen-alkali reactions will be defined.

EXPERIMENTAL

PULP AND SPENT LIQUOR SAMPLES

Pulps and spent liquors used in this project were generated as an integral part of a concurrent pulping study (Project 3264) (1). The pulps and spent liquors were stored at 5°C until used. The pulps, as provided, had oven-dry contents of ca. 25 to 30%. Portions of the pulp samples were air dried in a forced-air oven and then Wiley milled using a No. 40 screen. Pulp samples used for preparation of the holocelluloses were never dried.

GENERAL

The methods for holocellulose preparation, neutral sugar analysis, and spent liquor fractionation were described previously (3). Nitrogen analyses were made using a semimicro Kjeldahl method (26) or were performed by Chemalytics, Inc. (2330 S. Industrial Park Dr., Tempe, AZ 85282). Ash contents of ultrafiltration retentates were determined by TAPPI method T 625 ts-64. Individual metals in the retentates were determined by atomic absorption or flame emission spectroscopy with sodium being determined by difference. Holocellulose viscosities were determined in cupriethylenediamine solutions (0.5%) according to TAPPI method T 230 os-76.

DEGREE OF POLYMERIZATION ANALYSIS

Chromatographic Analysis

Liquid chromarographic analyses (LC) were performed on a Varian 8500 chromatograph equipped with a gas-activated loop injector. A Perkin-Elmer LC-55 spectrophotometer equipped with a flow cell was used as the detector. Four Styragel columns (Waters Associates) having permeability ranges of 10^6,

10^5, 10^4, and 10^3 A were linked in series and adapted to fit the Varian chromatograph. The Styragel columns were recalibrated, essentially as described previously, with eleven "monodisperse" polystyrene standards with molecular weights ranging from 2.1×10^3 to 3.6×10^6. Analyses were performed at ambient temperature using tetrahydrofuran as the elution solvent at a flow rate of 2.0 ml min^{-1}. Detector wavelengths of 225 and 235 nm were used for analyzing polystyrene and polysaccharide percarbanilate, respectively.

Tetrahydrofuran was purified for LC use by refluxing it with lithium aluminum hydride and then fractionally distilling it through a 40-cm column packed with Raschig rings (27).

Liquid-chromatographic analysis of tetrahydrofuran solutions (ca. 0.25%) of the polysaccharide percarbanilates were made using an internal reference as described previously (3).

Analysis of the LC chromatograms was essentially as described previously (3) with the exception that the baseline was defined as the line between a point on the elution curve as close to a $V_s - V_i$ value of 10 (DP ≃ 3) as possible and the start of polymer elution.

Cellulose Tricarbanilate Stability

Cellulose tricarbanilate (0.9 g) (3) was dissolved in anhydrous pyridine (125 ml) which had been boiled briefly. Phenyl isocyanate (18 ml) was added to the solution, and the flask was suspended in a constant temperature bath at the desired temperature. The solution was stirred with a sealed overhead stirrer. Samples (25 ml) of the solution were withdrawn at periodic intervals. Methanol (4 ml) was added to the sample to react with the phenyl isocyanate. The sample was diluted with dioxane (10-15 ml) to reduce the

viscosity and vacuum filtered through two glass filter pads (Reeve Angel 934AH). The filtrate was poured in a very fine stream into a stirred solution of methanol (200 ml) and acetic acid (5 ml). The precipitated polymer was allowed to settle and the supernatant was siphoned from the mixture. The polymer was then washed with water (200 ml) and acetic acid (5 ml), washed with water (200 ml), and freeze-dried.

Holocellulose Derivatization

The freeze-dried holocellulose (3) was dried at least overnight *in vacuo* over phosphorus pentoxide. Anhydrous pyridine (100 ml) (27) was added to the dried holocellulose (0.1 g) in a 4-oz narrow-neck bottle. Phenyl isocyanate (7.2 ml) was added to the mixture, and the bottle was sealed with a Teflon-lined cap. Two of the reaction bottles were sealed in a stainless steel laboratory digester of slightly larger diameter. The digester was rotated at *ca.* 3 rpm in an oil bath at 80°C for 2 days. The reaction mixture was allowed to cool slightly and methanol (3.3 ml) was added to react with the excess phenyl isocyanate.

The reaction mixture was centrifuged, and the supernatant was carefully decanted and mixed with an equal volume of dioxane. The mixture was filtered through dry, washed sand over two glass filter pads. The filtrate was diluted with 10-20% dioxane and poured in a fine stream into a stirred solution of methanol (800 ml) and acetic acid (5 ml). The precipitated polymer was allowed to settle and the supernatant was siphoned from the mixture. The polymer was then washed with water (800 ml) containing acetic acid (5 ml), washed with water (800 ml), and freeze-dried.

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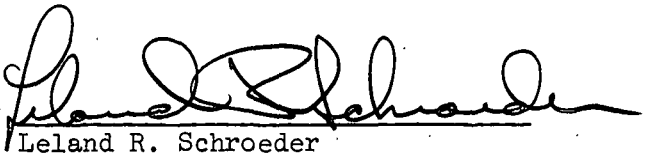

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